

III. "Zirconium and its Atomic Weight." By G. H. BAILEY, D.Sc., Ph.D., The Owens College. Communicated by Sir HENRY ROSCOE, V.P.R.S. Received April 15, 1889.

The investigation described in the following paper was undertaken primarily with a view to the redetermination of the atomic weight of zirconium. In previous determinations the sulphate had been used by Berzelius ('Poggendorff, Annalen,' vol. 4, p. 126) and Mats Weibull ("Om Zirkonium och dess föreningar"), the chloride and oxychloride by Hermann ('Journ. Prakt. Chem.,' vol. 31, p. 77), and the double fluoride of potassium and zirconium by Marignac ('Annales de Chimie,' vol. 60, 1860, p. 270). The results of these determinations are summed up in the following table, the relation $O : H = 15.96 : 1$ being used in the calculations.

	Mean deter- mination.	Maximum.	Minimum.	Author.
$Zr(SO_4)_2 : ZrO_3 \dots\dots$	89.23	89.42	89.05	Berzelius.
$Zr(SO_4)_2 : ZrO_2 \dots\dots$	89.255	90.158	88.97	Mats Weibull.
$Zr : Cl_4 \dots\dots$	88.56	Hermann.
$ZrO_3 : HCl \dots\dots$	89.915	90.76	89.07	„
$K_2ZrF_6 : K_2SO_4 \dots\dots$	90.31	92.57	89.84	Marignac.
$ZrO_3 : K_2SO_4 \dots\dots$	90.47	90.97	90.02	„
$K_2ZrF_6 : ZrO_2 \dots\dots$	90.6	91.1	89.7	„

The sulphate is somewhat readily decomposed by heat, the chloride and oxychloride are known to be unstable, and liable to considerable variation of composition according to the method of preparations, and the conditions under which these variations of composition are brought about were not understood, except in so far as the researches of Troost and others have indicated the great tendency which they show to pass into volatile and non-volatile oxychlorides of complicated character.

The determination is rendered difficult and unsatisfactory in consequence of—

- (a.) The difficulty of obtaining pure zirconia, and its separation from iron, titanium, and from silica.
- (b.) The tendency to form basic salts, and the hygroscopic character of its salts, and their general instability.
- (c.) The tenacity with which the hydrated zirconia retains the alkalies and smaller quantities of impurities in general.

Under these circumstances it seemed to me essential that any determination of the atomic weight of this element should be preceded by an inquiry into the best method of preparing pure zirconia, and an examination of the salts which might be made use of for the purpose, especially with reference to their stability.

Preparation of Crude Zirconia.

The raw material consisted of about 300 grams of zircons from North Carolina, for which I was indebted to the kindness of Sir Henry Roscoe, and in addition to this a quantity of impure zirconia. The zircons were powdered by heating them to redness, and then throwing them quickly into cold water; they were then roughly powdered in an iron mortar, and finally in an agate mortar, and passed through linen. Part of this was treated with hydrogen potassium fluoride, the product being extracted with water and recrystallised many times from hot water. Prepared in this way, however, the zirconia was still impure, and showed the presence of iron in small quantities, and in addition to this it was extremely difficult to get rid of alkali.

The methods of fusion with sodium carbonate or acid potassium sulphate are troublesome and even less satisfactory.

Ultimately caustic soda and sodium fluoride were adopted for breaking up the zircons as recommended by Linnemann, and a modified form of the process followed out by him ('Monatsh. f. Chem.,' vol. 6, p. 337) was adopted as the most convenient. A mixture of 100 grams of caustic soda and 10 grams of sodium fluoride is heated in a covered silver dish over a large Bunsen burner, 25 grams of finely powdered zircons are added in portions, the melt being kept stirred, and the heating continued for about an hour or so long as there is any effervescence. The resulting mass is broken up and extracted with water, the residue consisting principally of sodium zirconate, but containing also silica and undecomposed zircon, oxide of iron, &c. This is now digested with dilute hydrochloric acid and filtered, the residue being subjected repeatedly to the same treatment. The acid solution containing the zirconium is evaporated to perfect dryness, and then exhausted with very dilute hydrochloric acid, and the silica filtered off. The process of solution and evaporation is repeated until the residue obtained dissolves completely in the acid. The impurity now present in the largest quantity is iron, and it was thought desirable to remove the bulk of this first. The hydrochloric acid solution is, therefore, evaporated to small bulk, and left to cool; the oxychloride of zirconium separates out in acicular crystals, leaving the iron in solution. The crystals are thrown into a funnel, and the liquid as far as possible removed at the pump, and the process of solution and separation of crystals in this way repeated several

times. On precipitation of the final products with ammonia the crude zirconia is obtained, which forms the starting point for further purification. In further operations, reagents (such as potassium or sodium salts) which could not be removed by volatilisation were avoided, and even at the present stage it was considered advisable to redissolve the zirconia in hydrochloric acid, and reprecipitate with ammonia three times in order to get rid of the bulk of the sodium salts.

Purification of the Crude Zirconia.

This crude zirconia, free from the impurities that occur in larger quantity, was dissolved in hydrochloric acid, and crystallised out as oxychloride. The aqueous solution of this, slightly acidulated, was treated with sulphuretted hydrogen for twenty-four hours; a gelatinous precipitate was obtained of a purplish-black colour, consisting principally of sulphides of silver and copper, together with some hydrated zirconia. To the filtrate saturated with sulphuretted hydrogen was now added a little ammonia, which had the effect of bringing down a little more zirconia, and also the small quantities of impurities precipitable by ammonium sulphide. The liquid was now acidulated and boiled down to get rid of the sulphuretted hydrogen, and excess of oxalic acid added to the concentrated solution to precipitate gadolinite earths, and finally treated with ammonium oxalate. There still remained some iron which had either not been removed or had been introduced in the course of treatment. To separate this the oxychloride was crystallised repeatedly from concentrated hydrochloric acid, and finally washed with a mixture of the acid with one part of alcohol and ten parts of ether. The only impurity that could now be detected was soda, which the zirconia retained with the greatest tenacity.

This was removed by precipitating the zirconia several times by means of ammonia, and redissolving it in hydrochloric acid. The zirconia finally precipitated by ammonia was washed* so long as any ammonium salts could be detected in the wash water.

The zirconia obtained was tested as to purity in the following way:—

- (1.) A portion treated with hydrofluoric acid showed no alteration in weight;
- (2.) The moist oxide dissolved completely in oxalic acid;
- (3.) On ignition it was perfectly white (inclined to a bluish cast), and a quantity exhausted with hydrochloric showed no trace of iron by the most delicate tests.

* Some of the earlier results had to be rejected because of incomplete washing. 20 grams of zirconia required to be washed 150 times at the pump before ammonia salts were got rid of, at least 50 litres of water being used in the process.

In order, however, to have a further guarantee that the product used for the determination of atomic weight had a definite composition and character, the experiments described later for the determination of atomic weight were made upon four portions, whose final treatment was as essentially different as possible.

Portion A was precipitated from an acid solution of the sulphate by the addition of hydrogen peroxide containing no other impurity than sulphuric acid.

Portion B was transformed into the tetrachloride by heating the zirconia with charcoal in a current of chlorine and then reprecipitated by ammonia.

Portion C was crystallised out from concentrated sulphuric acid by boiling off part of the excess of acid and then allowing to cool.

Portion D was further recrystallised from hydrochloric acid and washed very thoroughly with a mixture of hydrochloric acid, alcohol, and ether as described.

Stability of the Zirconium Salts.

In the case of zirconium it was evident that the number of compounds of a simple character and of sufficient stability to afford a good basis for a determination of atomic weight must be very limited. The principles, therefore, on which it was decided to proceed were—

- (a.) To prepare zirconia by several independent methods.
- (b.) To ascertain the most stable salt (or salts if more than one should prove stable), and the most simple transformation of this which would lead to an accurate determination.

Indeed it seems to me in general that unless there are two or more salts of a very stable character, that reliance should lean rather towards the production of the raw material by independent processes, than towards the confirmation of results obtained from a more stable salt by means of values derived from observations on one that is less stable.

The methods previously used in the determination involved—

- (1.) Relation of zirconium sulphate to oxide.

- (a.) Direct conversion by ignition.
- (b.) *Viâ* BaSO₄ by precipitation.

Mats Weibull (*loc. cit.*); Berzelius ('Pogg. Ann.,' vol. 4, p. 126).

- (2.) Relation of Zr (in ZrO₂) to Cl (in AgCl).

- (a.) By analysis of ZrCl₄.
- (b.) By analysis of ZrOCl₃.

Hermann ('Journ. Pr. Chem.,' vol. 97, p. 323).

(3.) Relation of K_2ZrF_6 to ZrO_2 and to K_2SO_4 . Marignac ('Ann. de Chim.,' vol. 60, p. 257).

In addition to these it seemed possible that the relations—

(4.) Zr to ZrO_2 by direct oxidation of the metal,

(5.) Zr (in ZrO_2) to Br (in AgBr) on analysis of $ZrBr_4$, might be worthy of examination.

The bodies, therefore, to be investigated were the metal, the oxide, the chloride, the oxychloride, bromide, sulphate, and double fluoride. With regard to the last mentioned, no further investigation was considered necessary after the very complete treatment it has received at the hands of Marignac following upon the work of Berzelius on the double fluorides.

Preparation and Properties of Zirconium.

Zirconium was first obtained by Berzelius ('Poggendorff, Annalen,' vol. 4, p. 117) by heating the anhydrous potassium zirconium fluoride with metallic potassium in an iron tube. It is described by him as being an amorphous black powder without lustre and resembling charcoal in appearance. Becquerel, by electrolysis of a concentrated solution of the oxychloride, and Troost ('Journ. Prakt. Chem.,' vol. 97, p. 171), by fusing together potassium zirconium fluoride and aluminium, obtained it in a crystalline form, though it does not seem to have been in either case quite pure. Phipson ('Journ. Prakt. Chem.,' vol. 96, p. 447) found that like carbon, boron, and silicon it can be obtained by heating together magnesium and zirconia and then extracting the excess of magnesium and the magnesia by means of dilute hydrochloric acid.

There was left a black amorphous powder resembling that described by Berzelius. No determinations are, however, given to show how far this was free from impurity, and whether it contained unreduced oxide. A repetition of Phipson's experiments showed that as far as the presence of foreign impurity is concerned it leaves nothing to be desired, though I have not succeeded in preparing the metal by this or any other of the methods in a state of sufficient purity for a determination of atomic weight. Phipson's method is a very convenient one for preparing the metal, and the following results will show the conditions most favourable to its production in this way.

Experiments were first tried with intimate mixtures of magnesium powder, 3 grams and 5 grams respectively, with 4.4 grams of zirconia, the mixture being heated to bright redness in an iron tube, the mouth of the tube being filled with finely powdered common salt. There remained, after repeated digestion with dilute hydrochloric acid, a fine black powder, so fine that it passed through the filter-paper and remained in part suspended for weeks in water, showing a reddish-purple coloration by transmitted light.

When dried and heated in air to a point far below redness it glowed and was transformed into zirconia with a small increase in weight. It evidently consisted of zirconia containing only a small percentage of the metal. When rubbed in an agate mortar, however, it showed no white particles, and the variability of its composition, as shown in these and other experiments, lent no support to the assumption that a lower oxide had been formed. In a second set of experiments, magnesium foil was used, and in this case the foil retained its form, although permeated by metallic zirconium exactly as it does in the reduction of carbon compounds. By separating the foil from the finer powder it was possible to obtain zirconium almost free from oxide. Three specimens were prepared: A resembled those already described, a velvety black powder, B had a slight greenish cast, and C a decided olive-green colour with a slight lustrous appearance.

It was thought, therefore, that A would prove to be the purest zirconium, judging from the experience of previous experimenters.

Samples were carefully heated in a stream of air, the moisture and carbonic acid (arising from carbon in the magnesium used) directly determined, and the proportion of Zr and ZrO_2 arrived at by calculation, knowing the original weight of substance taken and the weight of ZrO_2 left in the boat.

A simply glowed and passed into a white powder as the previous specimens had done, B burnt with a white light much more brightly than A had done, and C gave out a dazzling light resembling in its brightness that of burning magnesium; when thrown into the flame of a Bunsen burner they gave beautiful white scintillations.

The results of the analysis gave the following composition:—

	A.	B.	C.
Metallic zirconium .	0.0453	0.1516	0.3383
Zirconia	0.3434	0.3561	0.0267
Moisture	0.0100	0.0086	0.0350
Carbon	0.0015	0.0013	nil

A careful examination showed that no iron or magnesium was present, and, indeed, after precipitation of the zirconia, the residual impurity from half a gram weighed less than a milligram, and consisted entirely of silica, introduced doubtless by the ammonia used in precipitation. Preparation C was, therefore, almost pure zirconium, containing only a slight admixture of oxide; rubbed up in an agate mortar it showed a brassy lustre. It is stated generally that zirconium is hardly acted upon at all by mineral acids or aqua regia, but dissolves in hydrofluoric acid. My own observations confirm these statements, with the exception that concentrated sulphuric acid begins to act in the cold even, and on gently warming the action pro-

ceeds rapidly with a copious evolution of sulphur dioxide, and even with the production of free sulphur.

Dilute sulphuric acid (1:1) acts more slowly with the evolution of hydrogen.

Zirconium is acted upon also by chlorine and bromine, in which, on gentle heating, it undergoes vivid combustion, forming the tetrahaloid derivatives, and this is, indeed, a convenient method for obtaining these bodies. The iodide could not be obtained. When the zirconium was filtered, after the digestion with dilute hydrochloric acid, and dried, it was found to have occluded hydrogen. This was removed by exposing it *in vacuo* for some days, and removing the hydrogen by the mercury pump.

The Oxides.—The only points for remark in addition to what has already been published, relate to the reduction (?) of zirconia and to the peroxide of zirconium.

With regard to the former it has already been noticed that when zirconia is heated, surrounded by the reducing flame of coal-gas, it blackens. This blackening is only superficial, however, and is in all probability due to a thin deposit of carbon, and it reoxidises readily to a white powder when heated in air, with a *decrease* of weight—small, indeed, but distinct. Heated at the highest temperature of the blowpipe flame in hydrogen, it undergoes no reduction.

Zirconium Peroxide, ZrO_3 .

Clève ('Paris Soc. Chim. Bull.,' vol. 43, p. 53) precipitated an oxide, to which he assigned the composition ZrO_3 , by adding ammonia and hydrogen peroxide to a solution containing a zirconium salt; my own experiments ('Chem. Soc. Journ.,' vol. 49, p. 481), in which the oxide was precipitated from a dilute solution by the addition of hydrogen peroxide alone, the solution being slightly acid, gave an oxide agreeing well with the composition Zr_2O_5 ; it was found also that an oxide resembling Clève's could be obtained without the addition of ammonia. In order to see whether the peroxide, ZrO_3 , was identical with that obtained by Clève, I precipitated a large quantity of a moderately concentrated solution of zirconium sulphate, containing a slight excess of acid—

(a.) By the addition of hydrogen peroxide alone.

(b.) By the addition of hydrogen peroxide, and then ammonia until just alkaline.

	Mean determinations.		Calculated for ZrO_3 .
	(a.)	(b.)	
Zr	64.92	64.97	65.21
O	35.08	35.03	34.79

It is evident, therefore, that with due precaution an oxide agreeing very definitely with the formula ZrO_3 , is obtainable by precipitation with hydrogen peroxide, either in alkaline or acid solution. The addition of ammonia, especially in excess, is, however, not to be recommended, since it tends to bring down the ordinary oxide, and to decompose the hydrogen peroxide added, with the production of nitrous and nitric acid. Dried for several weeks over phosphorus pentoxide, the oxide became constant in weight and showed the composition $\text{ZrO}_3 \cdot 3\text{H}_2\text{O}$, the hydrate of zirconia being $\text{ZrO}_2 \cdot 2\text{H}_2\text{O}$. The salt, however, lost about 2 per cent. of oxygen during the process of drying, and if this was carried out at 100° it had the composition Zr_2O_5 .

Zirconium Tetrachloride.

About 30 grams of this salt were prepared in the usual way, by passing dry chlorine over a mixture of charcoal and zirconia. If a determination was to be made from this salt some process of purification was necessary, and a criterion that a body of constant composition had been obtained, especially as it is known that volatile oxychlorides exist.

For this purpose a combustion-tube, in which the chloride was prepared, was drawn out into a series of bulbs, separated by constrictions. The chloride was then sublimed (a lower temperature being used for each successive bulb) in a current of dry chlorine into these bulbs, which were separately sealed off and their contents analysed. It was hoped in this way that two or more bulbs would be obtained showing concordant results, but notwithstanding that every precaution was taken to exclude air and moisture, no such result could be achieved, and decomposition was clearly indicated to have taken place with the formation of traces of a reddish-brown product, the equivalent of chlorine in relation to zirconium being in some cases higher and in others lower than four to one. Furthermore, in no case was it found possible to prepare such a product perfectly free from silica or iron. It seems, indeed, that zirconium tetrachloride is even more liable to dissociation and decomposition than the corresponding silicon compound.

Zirconium Oxychloride.

This salt is prepared, as already stated, by crystallisation from concentrated hydrochloric acid. The difficulties attending its preparation in the pure state arise from the presence of free hydrochloric acid and from the readiness with which the salt passes into oxychlorides of a more basic character. Berzelius attempted to remove the excess of free acid by heating the salt to 60° , but was not able to obtain a definite product, his numbers being—

The whole of the specimens analysed dissolved in water to a clear solution, with a slightly acid reaction. The determination which

shows the highest proportion of chlorine would give the atomic weight of zirconium as 92, which is undoubtedly too high, and, moreover, it will be quite evident from these numbers that no trustworthy determination was to be expected from this salt.

The Tetrabromide.

This salt was prepared by heating zirconia in an atmosphere of bromine vapour, but proved no more promising in its behaviour than the corresponding chlorine derivative.

The Sulphate.

Several methods of preparing the sulphate were tried, but ultimately that originally used by Berzelius was adopted. Finely powdered zirconia (air-dried) was heated with concentrated sulphuric acid, and most of the excess of acid driven off at as low a temperature as possible. In order to obtain the normal sulphate Berzelius drove off the excess of sulphuric acid, and then heated for a quarter of an hour, but never to redness; Mats Weibull heated till constant at 300°, a temperature manifestly too low. Clève, in a private communication, advised me to heat in a sulphur bath (442°). It seemed, however, that in this instance, where the atomic weight depended on determinations from the sulphate alone, and especially since this is a general method applicable to several other elements, it was desirable that the limits of temperature within which the normal sulphate was stable ought to be ascertained. This was done in the case of a number of sulphates (Bi, Mg, Zn, Di), and the details of the investigation have already appeared ('Chem. Soc. Journ.,' vol. 51, p. 676).

The salt containing excess of sulphuric acid was heated in a bath, described in that communication, which could be easily kept within 5°, and at any temperature up to 500°. The boat containing the salt was weighed from time to time until it became nearly constant. The salt was then finely powdered, and the heating continued in periods of about four hours, until no further diminution of weight occurred, showing that the free sulphuric acid had been got rid of. The temperature of the bath was now raised by intervals of about 10°, and the heating continued for several hours at each limit, weighings being made after each increment until a point was arrived at at which loss of weight was again observed. This indicated that the temperature had been attained at which the normal salt began to undergo decomposition. We have then the limits of temperature within which the normal sulphate is stable. Several series of determinations were made, and one of these is given to show the character of the values obtained.

			Grams.
Weighing tube and boat			20·64962
" " and salt			22·9095
After heating 6 hours at 300°			22·9045
" 7 " 330			22·9015
" 4 " 350			22·9002
" 4 " 365			22·90012
" 5 " 380			22·90025
" 4 " 390			22·90020
" 4 " 410			22·89820

The above numbers have not had applied to them the small corrections for variations of barometer and thermometer, and no importance need be attached to the differences of one or two tenths of a milligramme between 350° and 400°.

It appears, therefore, from these experiments that zirconium sulphate is stable up to 400°, and that the excess of sulphuric acid is driven off completely at 350°. If, therefore, a mixture of the salt and the free acid, prepared as above, be heated at any temperature between 350° and 400° till constant, we shall obtain the normal sulphate. The temperature of the sulphur bath would be too high, and of course at dull redness decomposition would set in.

The Atomic Weight of Zirconium.

After what has been said it may appear that the previous determinations of atomic weight from the sulphate would be too high rather than too low, since there can be little doubt that Berzelius heated the salt above 400°. It does not follow, however, that by heating it for a short time at a moderately high temperature more than a small fraction of the salt would be brought under conditions favourable to decomposition, nor even would the temperature of the mass be such that the whole of the free sulphuric acid would be got rid of. And the fact that on repeating such a treatment no variation in weight occurred, would be no guarantee that the salt was normal zirconium sulphate. My own experiments show that to get rid of the excess of acid requires prolonged heating, and at the same time renewal of the atmosphere in the vessel containing the sulphate. Apropos of this, Berzelius's precaution to introduce into the crucible in the last stage of the ignition of the sulphate a little ammonium carbonate is a very necessary one, as it displaces often 2 or 3 milligrams of sulphuric acid, which otherwise seems to remain in the crucible time after time and fix itself in the zirconia, when the crucible begins to cool. Furthermore, whatever previous experience may have been (for no special precaution is mentioned in any case), I have found it most difficult to ignite zirconium sulphate without loss; the decomposition occurs

with such violence at first, and the resulting zirconia is so extremely light that, though every care was taken, varying results were got, even in igniting very gently over the bunsen burner, some as low as 43 per cent. of oxide instead of 43.3 at least. On carefully watching, it was seen that minute particles of zirconia were being carried out of the crucible, although the cover fitted well. This loss was only avoided by enclosing the crucible within a second larger one, whose cover fitted quite closely and only communicated with the external atmosphere by a drawn-out neck, so that there were no air-currents. Even then, if the crucible was placed over the blowpipe flame at once, loss occurred and it was necessary in every case to commence the operation over the flame of a bunsen burner, and then after half an hour to transfer to the blowpipe.

Part of the determinations were made by Berzelius in the wet way—that is, the zirconia was first precipitated by means of ammonia, and then the sulphuric acid determined in the filtrate by precipitation with barium chloride.

Having satisfied myself by careful comparative experiments that the results of both methods, under favourable conditions, correspond, I decided to adopt the dry method, viz., that of conversion of the sulphate into the oxide by ignition—

- (a.) Because it involved the least complicated operations and the fewest assumptions.
- (b.) Because under some circumstances basic zirconium sulphate is thrown down when ammonia is added to a solution of the sulphate.

In the following paragraphs are given the determinations of Berzelius and Mats Weibull from the sulphate, followed by those based upon my own experiments.

Berzelius's Determination ('Pogg. Ann.,' vol. 4, p. 126).

From the analysis of the sulphate:—

SO ₃ :	ZrO ₂ ::	100 :	75.84
„	„	:	75.92
„	„	:	75.80
„	„	:	75.74
„	„	:	75.97
„	„	:	75.85

Mean 75.853

ZrO ₂ :	2SO ₃ ::	1.5171 :	2
Zr	: O	::	5.591 : 1
Zr	: H	::	89.23 : 1

Mats Weibull's Determinations.

$\text{Zr}(\text{SO}_4)_2$.	ZrO_2 .	$\frac{\text{ZrO}_2}{\text{Zr}(\text{SO}_4)_2}$.
1·5499 grams.	0·6684 gram.	43·126 per cent.
1·5445 „	0·6665 „	43·153 „
2·1683 „	0·9360 „	43·168 „
1·0840 „	0·4670 „	43·081 „
0·7913 „	0·3422 „	43·321 „
0·6251 „	0·2695 „	43·113 „
0·4704 „	0·2027 „	43·091 „
Total .. 8·2335 grams.	3·5523 grams.	43·146 per cent.

Mean determination :—

Zr : O :: 5·592 : 1

Zr : H :: 89·255 : 1

My own Determinations.

$\text{Zr}(\text{SO}_4)_2$.	ZrO_2 .	$\frac{\text{ZrO}_2}{\text{Zr}(\text{SO}_4)_2}$.
<i>Portion A.</i>		
2·02357 grams.	0·87785 gram.	43·381 per cent.
2·6185 „	1·1354 „	43·360 „
<i>Portion B.</i>		
2·27709 grams.	0·98713 gram.	43·350 per cent.
2·21645 „	0·96152 „	43·385 „
<i>Portion C.</i>		
1·75358 grams.	0·76107 gram.	43·4016 per cent.
1·64065 „	0·7120 „	43·397 „
<i>Portion D.</i>		
2·33255 grams.	1·01143 grams.	43·361 per cent.
1·81105 „	0·78485 „	43·337 „
Totals .. 16·67344 grams.	7·23125 grams.	43·37 per cent.

Maximum Zr : O :: 5·674 : 1

Zr : H :: 90·559 : 1

Minimum Zr : O :: 5·654 : 1

Zr : H :: 90·237 : 1

Mean Zr : O :: 5·664 : 1

Zr : H :: 90·401 : 1

Corrections in the Weighings.

The balance used could be read directly to $\frac{1}{50}$ milligram, and had been proved to be a most reliable instrument. The weights were an excellent set by Staudinger of Giessen, and showed an average variation from the normal amounting to only 0.000035 gram.

Corrections were introduced—

- (a.) For the weights.
- (b.) For displacement of air and variations in temperature and pressure.
- (c.) For variations arising by reason of the different hygroscopic conditions of the desiccator and balance case.

In any case where condensation of moisture was liable to occur this was corrected for by noting the increment of weight per minute for several minutes whilst exposed in the balance case, and then constructing a curve, with increment of weight and time as ordinate and abscissa, from which the necessary correction at the time of weighing could be introduced. In nearly all cases over 2 grams of the sulphate was used for each determination, and even with 2 grams a difference of 1 milligram in the weight of the zirconia obtained implies a difference of 0.25 in the atomic weight; it is, therefore, evident that in some previous determinations, where less than a gram has been taken, there is considerable risk of error in the atomic weight.

IV. "Magnetic and other Physical Properties of Iron at a High Temperature." By JOHN HOPKINSON, F.R.S. Received April 16, 1889.

(Abstract.)

This paper deals with the same subjects as are dealt with in three short papers* already read before the Royal Society. It gives full particulars of the experiments made, both on the samples there mentioned and on other samples.

V. "Determining the Strength of Liquids by means of the Voltaic Balance." By G. GORE, LL.D, F.R.S. Received April 17, 1889.

* 1. "Magnetisation of Iron at High Temperatures." (Preliminary Notice.) 'Roy. Soc. Proc.,' vol. 45, p. 318. 2. "Recalescence of Iron." *Ibid.*, p. 455. 3. "Electrical Resistance of Iron at a High Temperature." *Ibid.*, p. 457.